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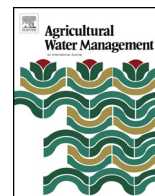
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Effects of tillage and application rate on atrazine transport to subsurface drainage: Evaluation of RZWQM using a six-year field study



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ABSTRACT

Well tested agricultural system models can improve our understanding of the water quality effects of management practices under different conditions. The Root Zone Water Quality Model (RZWQM) has been tested under a variety of conditions. However, the current model's ability to simulate pesticide transport to subsurface drain flow over a long term period under different tillage systems and application rates is not clear. Therefore, we calibrated and tested RZWQM using six years of data from Nashua, Iowa. In this experiment, atrazine was spring applied at 2.8 (1990–1992) and 0.6 kg/ha/yr (1993–1995) to two 0.4 ha plots with different tillage (till and no-till). The observed and simulated average annual flow weighted atrazine concentrations (FWAC) in subsurface drain flow from the no-till plot were 3.7 and 3.2 µg/L, respectively for the period with high atrazine application rates, and 0.8 and 0.9 µg/L, respectively for the period with low application rates. The 1990–1992 observed average annual FWAC difference between the no-till and tilled plot was 2.4 µg/L while the simulated difference was 2.1 µg/L. These observed and simulated differences for 1993–1995 were 0.1 and 0.1 µg/L, respectively. The Nash–Sutcliffe model performance statistic (EF) for cumulative atrazine flux to subsurface drain flow was 0.93 for the no-till plot testing years (1993–1995), which is comparable to other recent model tests. The value of EF is 1.0 when simulated data perfectly match observed data. The order of selected parameter sensitivity for RZWQM simulated FWAC was atrazine partition coefficient > number of macropores > atrazine half life in soil > soil hydraulic conductivity. Simulations from 1990 to 1995 with four different atrazine application rates applied at a constant rate throughout the simulation period showed concentrations in drain flow for the no-till plot to be twice those of the tilled plot. The differences were more pronounced in the early simulation period (1990–1992), partly because of the characteristics of macropore flow during large storms. The results suggest that RZWQM is a promising tool to study pesticide transport to subsurface drain flow under different tillage systems and application rates over several years, the concentrations of atrazine in drain flow can be higher with no-till than tilled soil over a range of atrazine application rates, and atrazine concentrations in drain flow are sensitive to the macropore flow characteristics under different tillage systems and rainfall timing and intensity.

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1. Introduction

After the first ten years of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program (1992–2001), Gilliom et al. (2006) concluded that predictive modeling is critical for the successful assessment of U.S. water quality because the expense of direct monitoring prevents the acquisition of data

at spatial and temporal resolutions required to manage water resources in a cost effective manner. Therefore, the current NAWQA Program heavily emphasizes the use of thoroughly tested models as a complement to monitoring. As part of this emphasis, one of the current goals of the NAWQA Program is to develop well tested models to predict pesticide transport from the land surface to the water table. Statistical models for pesticides in ground and surface water have been developed within the NAWQA Program (e.g., Stackelberg et al., 2012; Larson and Gilliom, 2001). However, the use of process based models for long-term prediction of pesticide fate and transport under subsurface drainage, macropore flow, and

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different management practices in the U.S. Midwest has thus far been limited.

In their summary of the NAWQA Program, Gilliom et al. (2006) reported that atrazine (and its metabolite deethylatrazine) was the single most frequently detected pesticide in streams and ground water, being detected greater than 90% of the time in streams and 42% of ground water samples in agricultural areas. In 1998 atrazine was detected in all 129 Midwestern stream and river water samples studied with median and maximum concentrations of 3.97 and 224 $\mu\text{g/L}$ (Battaglin et al., 2000). Frequent detection of this herbicide is partly related to its high usage rate with approximately 23 million kg of atrazine applied to corn in the United States in 2010 (USDA, 2012). This high detection frequency may affect reproduction of aquatic flora and fauna, which impacts the whole aquatic ecosystem (e.g., Graymore et al., 2001). Concentrations of atrazine were greater than one or more aquatic-life benchmarks in 18% of agricultural streams in the multi-year national study (Gilliom et al., 2006). Furthermore, because drinking water with excessive levels of atrazine for many years could lead to cardiovascular system or reproductive difficulties, the Environmental Protection Agency set a maximum contaminant level (MCL) of 3 $\mu\text{g/L}$ (USEPA, 2012).

Subsurface drains generally reduce pesticide transport in surface runoff because of increased infiltration (Kladivko et al., 2001). Also, the NAWQA Program found that the atrazine concentration in ground water was inversely correlated with artificial drainage, perhaps because drains divert atrazine to streams and rivers reducing atrazine transport below the “tile” drain depth (Stackelberg et al., 2012). Although subsurface drains can reduce atrazine transport in runoff and to ground water, atrazine is detected in streams at high concentrations in corn-belt states where it is heavily applied including Iowa, Illinois, Indiana, and western Ohio (Gilliom et al., 2006). Subsurface drains are also prevalent in these states (e.g., Jaynes and James, 2007).

Effective methods to reduce pesticide loss to subsurface drainage and leaching include application rate reduction, product substitution, and shift of the application date. However, the effects of tillage systems on pesticide transport are inconsistent, insufficiently known, and unpredictable (e.g., Reichenberger et al., 2007). The Root Zone Water Quality Model (RZWQM) is an agricultural system model that includes routines to simulate pesticide transport to subsurface drains, subsurface soil, shallow ground water, and macropore flow. Malone et al. (2003, 2004b) found that RZWQM successfully simulated the effects of tillage systems on pesticide transport: (1) using data from undisturbed soil blocks brought into the laboratory and (2) using data from a single season field study on a well drained soil. The associated model parameterization methods to simulate the effects of tillage systems on pesticide transport have not been tested for soils with subsurface drainage using multiple years of data.

In complex systems such as agriculture, models have been suggested as the only way to quantify the site specific effects of management practices across the array of interacting conditions often affecting the system (Ahuja et al., 2002). Malone et al. (2004c) concluded that in general RZWQM simulates pesticide fate reasonably well under many scenarios after extensive calibration and testing. However, field assessments of RZWQM simulated pesticide concentration in subsurface drainage under different application rates are lacking. In fact, little field research is available reporting pesticide concentrations in subsurface drainage under multiple application rates.

Pesticides can rapidly move from the soil surface to ground water due to preferential flow (e.g., Arias-Estevéz et al., 2008). Goss et al. (2010) suggested that providing evidence of this mechanism is one of the most significant roles lysimeters have provided toward the development of our understanding of ground water contamination. Preferential flow has been defined as ‘...all phenomena

where water and solute move along certain pathways, while bypassing a fraction of the porous matrix’ (Clothier et al., 2006; Hendrickx and Flury, 2001). Recently, Tiktak et al. (2012) needed to modify the leaching model PEARL to include preferential flow to accurately simulate the rapid movement of pesticides to subsurface drainage. Likewise, Guzman and Fox (2012) showed that accurately representing preferential flow is very important to model pathogen and *E. coli* transport to subsurface drains using RZWQM.

Although more research is needed on the subject, RZWQM has been used to investigate the effects of tillage systems and preferential flow on atrazine movement in artificial subsurface drainage. Kumar et al. (1998) concluded that RZWQM showed high potential for predicting atrazine losses with subsurface drainage as affected by tillage systems when macropore flow was simulated. They reported higher simulated and observed atrazine loss to drain flow under no-till compared to moldboard plow systems, which was attributed to higher lateral saturated hydraulic conductivity under no tillage. Atrazine loss to drain flow is the product of atrazine concentration in drainage and drain flow volume. Therefore, the lateral saturated conductivity could affect the drain flow volume more than the atrazine concentrations in drain flow. Malone et al. (2003) attributed higher simulated and observed pesticide concentrations in leachate under no-till compared to tilled soil to parameters affecting the timing of macropore flow during rainfall. Because macropore flow occurred sooner after rainfall initiation in the no-till treatment, the result was higher pesticide concentrations in leachate.

The pesticide component of RZWQM was thoroughly revised subsequent to the initial release in 1992 (Wauchope et al., 2004). Concurrent with this revision, the model was tested using short-term field data under conditions without subsurface drainage (Malone et al., 2004b,c; Ma et al., 2004a). Few long term field tests (e.g., >3 years) of the revised pesticide component of RZWQM have been conducted and one of the only tests of the revised model under subsurface drainage used two field sites in Indiana with one year of data for model calibration and testing (Fox et al., 2007).

Investigating agricultural system model parameter sensitivity has been an important component of many research projects (e.g., Kumar et al., 1998; Ma et al., 2004b; Walker et al., 2000; White and Chaubey, 2005; Ahmed et al., 2007). Malone et al. (2001, 2004b) reported that the macropore parameters were among the most sensitive RZWQM inputs affecting simulated atrazine and metribuzin transport through well drained soil. In contrast, Kumar et al. (1998) found soil macroporosity among the least sensitive variables associated with RZWQM simulation of atrazine transport through poorly drained soil to subsurface drain flow. Few studies, however, have investigated the sensitivity of a wide range of RZWQM input parameters associated with simulated pesticide concentrations in subsurface drain flow. To facilitate model parameter optimization and sensitivity analysis, RZWQM was recently linked with the automatic parameter optimization program PEST (model independent parameter estimation; Doherty, 2004) that reports sensitivity indices of optimized parameters (Malone et al., 2010; Nolan et al., 2010). An additional benefit of using automatic calibration methods such as PEST is that they help provide an objective, defensible, and repeatable way to calibrate models with many parameters (Rose et al., 2007).

As discussed, management practices such as application rates and tillage systems can influence pesticide transport through soil, but the affect on pesticide transport to subsurface drainage is poorly understood. RZWQM can accurately simulate pesticide transport through macropores and has been tested under a variety of conditions, but the current model’s ability to simulate pesticide concentrations and transport in subsurface drain flow over a long

term period under different tillage systems and pesticide application rates is unclear. Therefore, our objective was to use RZWQM to evaluate atrazine transport through poorly drained soil to sub-surface drain flow under two tillage systems and different atrazine application rates. The revised pesticide component of RZWQM was tested using the same three-year dataset as Kumar et al. (1998) along with three additional years when atrazine was applied at a reduced rate. As part of this study we conducted a sensitivity analysis of the PEST optimized model parameters.

2. Materials and methods

2.1. RZWQM description

The RZWQM pesticide, macropore, subsurface drainage, and other soil/water components have been described in detail (e.g., Fox et al., 2004; Malone et al., 2003, 2004b). A brief description of these processes is included here so that the model parameterization and discussion are comprehensible. The RZWQM is a one-dimensional (vertical) model that simulates plant growth and movement of water, nutrients, and pesticides in surface runoff, through the soil profile, into ground water, and through subsurface drainage. Drainage flux is calculated using an adaptation of the Hooghoudt equation (e.g., Fox et al., 2004; Malone et al., 2007). RZWQM simulates water and pesticide movement during rainfall or irrigation in the following steps:

- rainfall, irrigation and chemicals are received by the soil surface, plant foliage and surface residue;
- rainfall or irrigation exceeding the soil matrix infiltration rate becomes overland flow and enters macropores;
- overland flow exceeding both the maximum macropore flow capacity and soil matrix infiltration rate becomes surface runoff;
- a portion of the chemicals on the top 2 cm of the soil, plant foliage, and crop residue are extracted and transferred to overland flow and macropore flow; and
- as chemicals move through the macropores they interact with the pore walls, and a portion of the water and chemicals radially infiltrate into the soil matrix.

Water infiltration into the soil matrix is simulated using the Green–Ampt equation and water is redistributed using the Richards' equation. Soil hydraulic properties are described with a modified Brooks–Corey equation. These infiltration and water redistribution equations were described in some detail by Malone et al. (2003) and can be solved if reasonable estimates are available for saturated hydraulic conductivity (K_s , cm/h), soil porosity, air-entry or bubbling suction (h_b , cm); pore size distribution index (PSD, dimensionless), and residual water content. For the current RZWQM assessment, the soil porosity and residual water contents were obtained from Ma et al. (2007a,b) using the same plots as the current study while the other parameters were calibrated for each plot as described below.

If the rainfall rate exceeds the soil matrix infiltration rate, the excess is considered overland flow and transported into macropores. The water entering macropores is evenly distributed among macropores. For input into RZWQM, Malone et al. (2001, 2003) recommended using “active” macroporosity, i.e., half of percolate-production macroporosity (P_{mac} , cm²/cm²)

$$P_{\text{mac}} = 0.5 * N_{\text{mac}} * \pi * R_{\text{mac}}^2 \quad (1)$$

where N_{mac} is the number of percolate producing macropores per soil area (cm⁻²) and R_{mac} is the average radius of macropores (cm). Chemicals in macropore flow react with the soil walls according to chemical partitioning. Water and chemicals vertically moving

through macropores mix and react with a user defined radial length of the macropore wall called the effective soil radius (ESR). An ESR of 0.6 cm was used here and has resulted in accurate RZWQM simulations for several conditions (Malone et al., 2001, 2003, 2004b). The soil volume surrounding macropores available for chemical sorption, WVOL, is then:

$$\text{WVOL} = \pi * 0.5 * N_{\text{mac}} * [(R_{\text{mac}} + \text{ESR})^2 - R_{\text{mac}}^2] \quad (2)$$

Chemicals are transferred from the soil surface to overland flow and macropore flow by rainfall impact, is assumed to occur within the top 2 cm of soil, and contribution decreases exponentially within this depth increment (0–2 cm). This can be expressed as the nonuniform mixing model,

$$M_{\text{ave}} = e^{-(B1)Z} \quad (3)$$

where M_{ave} = average degree of mixing for depth increment between rainfall and soil solution (unitless); $B1$ = the non-uniform mixing parameter (cm⁻¹); Z = center of depth increment (0.5 or 1.5 cm).

2.2. Field study

Field data was collected at Iowa State University's Northeast Research Center near Nashua, Iowa. For our objectives, two plots (#13 tilled and #14 no-till) were used with atrazine applied in the spring of corn years at 2.8 kg/ha a.i. (1990–1992) and 0.6 kg/ha a.i. (1993–1995). Dates of atrazine application were May 2, 1990; May 28, 1991; May 6, 1992; May 17, 1993; May 2, 1994; and May 16, 1995. Corn was planted each May except 1994 when the no-till plot was planted to soybean and atrazine was not applied. Plot 13 was tilled with moldboard plow from 1990 to 1992 and chisel plow from 1993 to 1995. In addition to the tillage systems and atrazine application rates of these two plots, these plots were chosen partly because they were adjacent to each other with minimal soil differences (e.g., Ma et al., 2007b).

The seasonal water table below the 0.4-ha plots fluctuates from approximately 20 to 160 cm. Subsurface drainage tubes/pipes (10 cm in diameter) were installed in the fall of 1979 at 120 cm depth and 29 m apart. The drain lines through the center of the plots were instrumented to measure drainage volume and collect samples. The predominant soils from these two plots are Floyd loam (fine-loamy, mixed, superactive, mesic Aquic Pachic Hapludolls), Kenyon silty-clay loam (fine-loamy, mixed, superactive, mesic Typic Hapludolls), and Readlyn loam (fine-loamy, mixed, superactive, mesic Aquic Hapludolls). These soils are moderately well to poorly drained, are developed in sediment overlying loamy glacial till, and belong to the Kenyon–Clyde–Floyd soil association.

Subsurface drainage water samples were collected three times a week (when “tiles” were draining) for the first 60 days after application and composited for weekly pesticide analysis. For the remainder of the year, sampling frequency was based on flow, but never exceeded once a week. Weather data (solar radiation, daily maximum and minimum temperature, and hourly rainfall) were obtained from an on-site weather station for most of the simulation period with missing data filled from nearby weather stations (Ma et al., 2007b). The rainfall data was revised somewhat from Ma et al. (2007b) using the Iowa Mesonet hourly rainfall for Nashua because close analysis suggested that a few storms were missed in 1993 (IEM, 2012). Additional details on the plots, instrumentation, and field experiment are in Kumar et al. (1998) and the associated references.

Soil cores 2.5 cm in diameter were collected two to four times a year for atrazine analysis; generally to a depth of 120 cm. These were divided into depth increments: 0–10, 10–20, 20–30, 30–45

and 45–60 or 30–60, 60–90, and 90–120 cm. Three cores were collected from each plot at each sampling event and the three samples from the same depth were combined to make one set of samples for each plot. Details of the soil sampling and analysis for atrazine are described by Weed et al. (1995) and Azevedo et al. (1997).

2.3. RZWQM parameterization, calibration, testing, and application

2.3.1. Model initialization

The RZWQM with a revised pesticide component (e.g., Wauchope et al., 2004) was initialized using the plot 13 and 14 parameters and ten soil layers from Ma et al. (2007a,b) for a study of crop production, subsurface drain flow, and nitrate dynamics. The top two layers were designated 0–8 and 8–41 cm to replicate the pesticide transport and macropore parameterization strategy of Malone et al. (2003). Malone et al. (2003) reported that the RZWQM soil parameters for the depth immediately below 8 cm were important to accurately simulate pesticide transport through macropores from undisturbed 30 cm deep no-till and moldboard plow soil blocks without artificial subsurface drainage.

The current simulation was started in 1986 to allow hydrology and pesticide in soil and shallow ground water to initialize prior to model calibration and testing using data from 1990 to 1995. Atrazine application was simulated to occur on May 2 at 2.8 kg/ha for 1986–1989.

2.3.2. Model parameter calibration and sensitivity

The first phase of model calibration was to optimize the tilled plot for weekly subsurface drain flow, weekly composite atrazine concentration in drain flow, and soil atrazine concentration at the different soil depths and dates over the six-year field study (1990–1995). All years were included in the parameter optimization for the tilled plot to achieve the best possible atrazine partition coefficient (K_{oc}) and first order half life ($t_{0.5}$). These parameters (K_{oc} and $t_{0.5}$) were used in the no-till plot simulation without optimizing. Parameters adjusted for optimization are listed in Table 1 and were constrained to a range of values similar to those measured at the site or reported in other related studies (e.g., Ma et al., 2007a; Malone et al., 2003; Moorman et al., 2001). The optimization combined both manual parameter adjustment and the automatic parameter estimation (calibration) program PEST linked to RZWQM which is described in detail by Malone et al. (2010) and Nolan et al. (2010). One of the advantages of utilizing PEST is that all 23 RZWQM input parameters listed in Table 1 could be adjusted simultaneously to minimize a multicriteria objective function composed of four different observation groups: weekly subsurface drain flow (cm); their composite atrazine concentrations ($\mu\text{g/L}$); atrazine concentrations in soil at several depth increments and 21 dates (mg/kg); and the total atrazine in the soil profile (kg/ha) at 21 dates. The last step of this phase of model calibration was to objectively optimize the tilled plot with PEST for the parameters listed in Table 1 and the multicriteria objective function, but soil parameters below the top 50 cm were excluded from this last phase of model calibration.

The Gauss–Marquardt–Levenberg optimization methodology as implemented in PEST has been criticized for being too easily trapped in local objective function minima (Doherty and Johnston, 2003). This disadvantage can be overcome by using an objective function that combines multiple criteria and suitable relative weights (Doherty and Johnston, 2003). One of the main benefits of local optimization methods is that they require a fraction of the run-time of global methods. The objective function ($\Phi(\beta)$) based

on parameter set (β) can be summarized as:

$$\Phi(\beta) = \sum_{i=1}^{n1} [W_{ac_df,i}(P_{ac_df,i} - O_{ac_df,i})]^2 + \sum_{i=1}^{n2} [W_{df,i}(P_{df,i} - O_{df,i})]^2 + \sum_{i=1}^{n3} [W_{ac_sd,i}(P_{ac_sd,i} - O_{ac_sd,i})]^2 + \sum_{i=1}^{n4} [W_{a_sp,i}(P_{a_sp,i} - O_{a_sp,i})]^2 \quad (4)$$

where subscript i =ith observation; O =observed values; P =simulated values; w =observation weights; subscript ac_df =weekly flow weighted atrazine concentration in drain flow ($\mu\text{g/L}$); subscript df =weekly drain flow (cm/day); subscript ac_sd =atrazine soil concentration at different soil depths (mg/kg); subscript a_sp =total atrazine in the soil profile (kg/ha); $n1$ – $n4$ =number of observations associated with each observation group. Weights were chosen so that no criterion was allowed to dominate the objective function: 80, 0.8, 1.0, and 0.5 were used for atrazine concentration in drain flow, volume of drain flow, soil atrazine concentration at different depths, and atrazine in the soil profile, respectively.

The calibrated K_{oc} and $t_{0.5}$ from the tilled plot were input for no-till and kept constant throughout the optimization. The no-till plot was then calibrated similar to till using a combination of both manual and PEST optimization. The last step of this phase of model calibration was to objectively optimize the no-till plot parameters listed in Table 1 using PEST and weekly composite atrazine concentration in drain flow over three years (1990–1992) and weekly subsurface drain flow amount over six years (1990–1995). Using the entire dataset for hydrology calibration was acceptable because our objectives did not include testing the hydrology component and we wanted to minimize the effect of errors in the hydrology simulation on simulating atrazine's fate and transport (e.g., Malone et al., 2004b). Soil atrazine concentrations and total amount in the soil profile were not used to calibrate the no-till plot because this was the validation dataset.

After the final PEST optimization steps described above, the annual average flow-weighted atrazine concentration in subsurface drain flow (FWAC) was slightly over predicted for both plots. Therefore, the final optimization step was to manually increase the number of percolate producing macropores per soil area (N_{mac}) to achieve similar simulated and observed average annual FWAC for 1990–1992 (no-till) and 1990–1995 (till). The final set of optimized parameters is defensible considering site-specific measurements and related literature sources (Table 1).

To simplify the model assessment, tillage was not directly simulated using the model. Instead, tillage effects were simulated using the objectively optimized soil parameters. If tillage is selected as a management option in RZWQM, soil and macropore parameters are automatically adjusted by the model.

After model optimization, the sensitivity of each model parameter was calculated. For brevity, we report parameter sensitivity based only on the observations in the atrazine concentration in drain flow group from the tilled plot. The relative composite sensitivities of each parameter (RCS_j) were computed as described by Hill and Tiedeman (2007):

$$RCS_j = s_j * |p_j| * m^{0.5} \quad (5)$$

where subscript j indicates the j th parameter, $|p_j|$ is the absolute value of the log 10 of the optimized j th parameter, m is the number of observations with nonzero weights, and s_j is the composite sensitivity of the j th parameter described by Doherty (2004) and

Table 1
Calibrated RZWQM input parameters and parameter sensitivity.

Parameter	No-till	Till	RCS ^a	Comments and justification concerning the calibrated parameters
Soil matrix saturated hydraulic conductivity (K_s , cm/h)	4.1 (0–8 cm) 9.1 (8–41 cm) 12.8 (41–50 cm) 12.0 (50–69 cm) 15.1 (69–89 cm) 5.0 (89–130 cm)	4.2 4.0 5.6 12 15.1 1.0	2.0 2.2	Within the range of measured (Ma et al., 2007a). Similar to the calibrated values, the measured K_s of the 40–90 cm depth was greater than the surface 0–20 cm (Ma et al., 2007a)
Pore size distribution index (PSD, dimensionless)	0.10 (0–8 cm) 0.06 (8–50 cm) 0.11 (50–89 cm) 0.10 (89–130 cm)	0.07 0.06 0.11 0.07	14.0 23.1	Within the range of measured (Ma et al., 2007a). Similar to the calibrated values, the measured PSD of the surface layer and the 50–89 cm depth were the greatest values.
Bubbling pressure (h_b , cm)	5.0 (0–8 cm) 5.2 (8–50 cm) 5.0 (50–89 cm) 2.0 (89–130 cm)	4.6 6.0 5.0 2.0	7.3 6.7	Similar to the measured values (Ma et al., 2007a)
Lateral hydraulic gradient (LHG, dimensionless)	1.0E–5	4.0E–5	17.2	Ma et al. (2007b) reported the LHG for plots 14 and 13 of 1.1E–5 and 1.7E–5, respectively. Therefore, the trend of greater LHG for no-till is similar to Ma et al. (2007b)
Surface crust K_s , cm/h	0.056	0.053	13.6	Greater than the RZWQM input values discussed as reasonable by Malone et al. (2004b) and equal to or less than measured values of Rawls et al. (1990)
Number of percolate producing macropores (N_{mac} , cm ^{–2})	0.020	0.034	29.1	Within the range of field tension infiltrometer measurements and laboratory measurements on undisturbed soil blocks (Malone et al., 2003). $N_{mac} = 2 \times$ “active” macropores
Macropore radius (R_{mac} , cm)	0.12	0.10	17.9	Within the range of previous RZWQM input on tilled and no-till soil (Malone et al., 2003)
Lateral saturated hydraulic conductivity (LK _s , cm/h)	5.4	5.0	5.5	Approximately half the value calibrated from Ma et al. (2007b)
Atrazine partition coefficient normalized for soil carbon (K_{oc} , ml/g)	244.5	244.5	100.0	Comparable to measured values for Nashua Iowa (Moorman et al., 2001). Measured K_{oc} values were 187 and 485 ml/g for 0–15 and 100–115 cm soil
Atrazine first-order half-life ($t_{0.5}$, day)	46.4	46.4	25.8	Comparable to the measured and RZWQM calibrated values for Nashua Iowa (Azevedo et al., 1997; Weed et al., 1995)
Express fraction (EXF; dimensionless)	0.03	0.03	1.5	Equal to the assumed fraction if all active macropores in vicinity of the drain were connected to the drain. Drain spacing is 29 m. $([0.5 \times 29]^{-1} \times 0.5 = EXF = 0.03$; Fox et al., 2004)
Non-uniform mixing factor (B1, cm ^{–1})	6.0	4.4	Not calibrated	See Malone et al. (2003)

^a The parameter sensitivity was obtained by inverse modeling for plot 13 (tilled soil) based on the weekly flow weighted atrazine concentration (FWAC) over the five year simulation. Relative Composite Sensitivity (RCS) is expressed as a percentage of the maximum relative composite sensitivity.

Nolan et al. (2010). The RCS measures the composite changes in model predictions based on a fractional change of a parameter value (Doherty, 2004). Here, we normalize RCS to the maximum value obtained for the parameters and express as percent.

2.3.3. Model testing

The calibrated model was tested using the no-till plot atrazine transport in subsurface drain flow from 1993 to 1995. Although not formally tested, results of hydrology are briefly discussed because of their influence on atrazine transport to drain flow. Similarly, Li et al. (2008) tested RZWQM for its estimate of the effects of cover crop treatments on drain flow nitrate loss while using the entire dataset to optimize the hydrology component. An additional reason we did not thoroughly test and discuss the hydrology component is RZWQM was previously thoroughly evaluated for simulation of hydrology at the Nashua site (e.g., Ma et al.) and has been thoroughly evaluated and deemed acceptable for simulation of drain flow using several different Iowa datasets (e.g., Thorp et al., 2007). In briefly discussing the annual drain flow simulations compared to observed data, we use the Root Mean Square Error (RMSE) as a performance indicator.

One of the main indicators used for model evaluation is the Nash–Sutcliffe efficiency (EF, Nash and Sutcliffe, 1970)

$$EF = 1 - \frac{\sum_{i=1}^n (P_i - O_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (6)$$

where \bar{O} is the mean of observed values, P_i are the model estimated values, O_i are the observed values, and n are the number of data pairs. Model simulations can be considered satisfactory under a monthly time step if $EF > 0.5$ (Moriasi et al., 2007). The value of EF when model estimates perfectly match observed data is 1.0. Values for EF less than zero indicate that the average of observed measurements were a better estimator than the model. Other applied indicators of model performance include plotting and/or discussing: observed and simulated soil atrazine concentrations; observed and simulated average annual FWAC differences between no-till and till plots; parameterization such as differences between tillage systems. The percentage of simulated values that lay within a factor of 2 and 5 of observed values have been used as the primary measure of the goodness-of-fit of pesticide simulations in tile flow and discussed as superior to EF for pesticide simulations

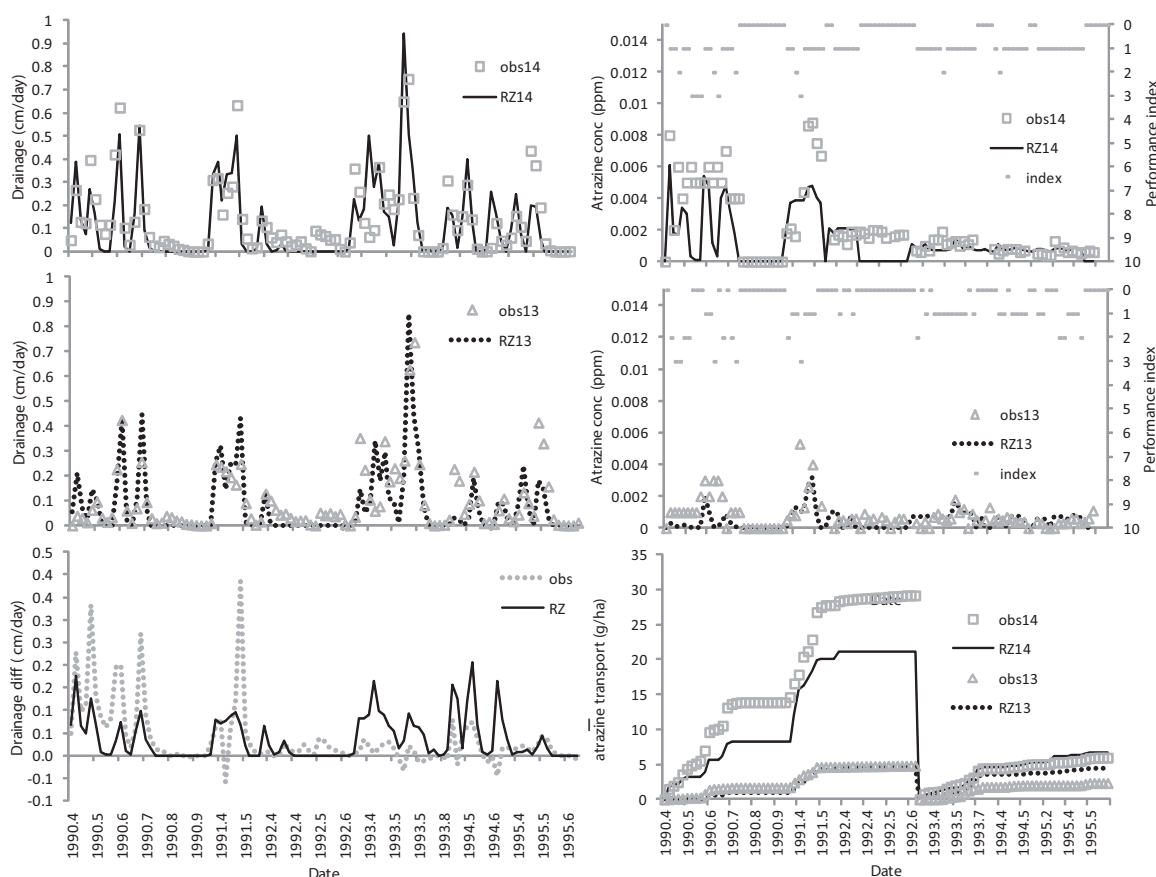


Fig. 1. Observed (obs) and RZWQM (RZ) weekly drain flow atrazine concentrations, atrazine flux, and drain flow amount. (a) is plot 14 drain flow. (b) is plot 13 drain flow. (c) is the drain flow difference between plots 14 and 13. (d) is plot 14 atrazine concentration. (e) is plot 13 atrazine concentration. (f) is cumulative atrazine flux in drain flow for 1990–1992 and 1993–1995. The performance index is zero if either the observed or simulated atrazine concentration is equal to zero. The performance index of 1, 2, and 3 indicates if the observed and simulated values are: within a factor of two (PI = 1), within a factor of five (PI = 2), exceed five (PI = 3). Plot 14 is no-till and plot 13 is moldboard plow (1990–1992) and chisel-plow (1993–1995). Note that the x-axis is scaled by sampling events and not time.

(Larsson and Jarvis, 1999). Other pesticide model evaluations have considered simulations near or within a factor of two times that observed good model performance (e.g., Malone et al., 2004b; Ma et al., 2000).

2.3.4. RZWQM simulations at different atrazine application rates

Some features of this field experiment added complexity to interpreting the data. For example, atrazine was applied at a rate of 2.8 kg/ha in 1990–1992 and 0.6 kg/ha in 1993–1995. Also, atrazine was applied to the tilled plot in 1994, but not to no-till. Therefore, we used the calibrated and tested RZWQM to study the effects of four atrazine application rates (0.5, 1.0, 2.0, and 3.0 kg/ha) under till and no-till systems when corn was planted each year from 1990 to 1995 and atrazine was applied at a constant rate each year throughout the six-year study.

3. Results and discussion

3.1. Model testing

3.1.1. Drain flow

Fig. 1a and b shows the weekly observed and simulated subsurface drain flow from 1990 to 1995. The Nash–Sutcliffe coefficient (EF) for weekly drain flow over the six-year study was 0.57 for the tilled plot and 0.64 for the no-till plot. Recent subsurface drain flow modeling research using RZWQM for nitrate or PESTDRAIN

for pesticides report EF values for drain flow between 0.62 and 0.84 (Malone et al., 2010) and 0.57 and 0.69 (e.g., Branger et al., 2009).

The average annual drain flow was under predicted by 1.4 and 3.7 cm/year for the no-till and till plots, respectively (Table 2), which is within 20% of observed. The RMSE was 4.0 and 5.6 cm for the no-till and till plots, respectively. Ma et al. (2007b) reported similar RMSE values at this same site for RZWQM simulations of annual tile drainage and commented that these values are close to the average RMSE for the measured drain flow data between replicates (5.7 cm).

The under predicted drain flow could be partly due to RZWQM over predicted runoff, RZWQM over predicted ET, or under reported rainfall input into RZWQM. Ma et al. (2007b) discussed that runoff may be over predicted at the Nashua Iowa site because RZWQM lacks a surface storage component. Also, RZWQM may have over predicted evapotranspiration at this site compared to field measurements (Ma et al., 2007b). Evapotranspiration (ET) is the sum of evaporation and transpiration listed individually in Table 3. Average annual RZWQM predicted runoff and ET were approximately 7 and 64 cm/year for both plots (Table 3), which were planted with continuous corn except in 1994 when the no-till plot was planted with soybean. Furthermore, Larsson and Jarvis (1999) report that the model MACRO may under predict drain flow because of errors in rainfall measurement due to wind drift, which may be under reported by 2–17%.

The calibrated model adequately simulated the pattern of weekly and annual drain flow differences between the two plots

Table 2Annual precipitation and observed and simulated drain flow, atrazine loss, and flow weighted atrazine concentration (FWAC) in drain flow.^a

Year	Prec. (cm)	Drain flow (cm)				Atrazine loss in drainage (g/ha)				FWAC ($\mu\text{g/L}$)			
		obs14	RZ14	obs13	RZ13	obs14	RZ14	obs13	RZ13	obs14	RZ14	obs13	RZ13
1990	118.8	28.2	23.0	11.8	15.0	13.9	8.2	1.7	0.9	5.3	4.2	1.9	1.2
1991	105.8	34.6	29.9	22.4	22.9	13.9	11.8	3.0	3.3	4.4	4.0	1.5	1.5
1992	84.4	16.5	11.0	15.9	8.5	1.4	1.2	0.2	0.4	1.6	1.3	0.6	0.6
1993	116.3	46.9	50.6	45.1	36.7	4.5	4.6	1.8	3.5	1.0	0.9	1.0	1.0
1994	86.3	8.6	10.6	8.1	2.4	0.6	0.7	0.2	0.2	0.7	0.9	0.6	0.8
1995	93.7	15.9	17.2	15.0	10.2	0.9	1.4	0.3	0.7	0.6	0.8	0.6	0.7
Average over several years													
1990–1992	103.0	26.4	21.3	16.7	15.5	9.7	7.1	1.6	1.5	3.7	3.2	1.3	1.1
1993–1995	98.8	23.8	26.1	22.7	16.5	2.0	2.2	0.8	1.5	0.8	0.9	0.7	0.8
1990–1995	100.9	25.1	23.7	19.7	16.0	5.9	4.6	1.2	1.5	2.3	2.0	1.0	0.9

^a Atrazine loss and flow weighted concentrations were calculated using dates where concentration was $\geq 0.5 \mu\text{g/L}$, which is close to the detection limit (lowest reported sample was $0.3 \mu\text{g/L}$). This calculation technique partially contributes to different observed flux compared to Kumar et al. (1998). Also, we calculate flux using weekly flow weighted concentrations while Kumar et al. (1998) calculated annual atrazine flux using average monthly concentrations. Drain flow was calculated using all data. Observed and RZWQM simulated data for plots 13 (till) and 14 (no-till) are obs13, obs14, RZ13, and RZ14.

Table 3

RZWQM simulated annual water budget, annual subsurface drain flow atrazine loss, and flow weighted annual atrazine concentration (FWAC).

Year	P (cm)	E (cm)	T (cm)	DS (cm)	TD (cm)	LF (cm)	RO (cm)	Atrazine loss (g/ha)	FWAC ($\mu\text{g/L}$)
Plot 13 (till)									
1990	118.8	22.8	51.0	0.0	15.0	12.9	11.7	1.0	0.7
1991	105.8	21.3	35.3	0.0	22.9	10.2	10.3	3.4	1.5
1992	84.4	15.8	45.4	0.0	8.5	10.4	4.9	0.8	0.9
1993	116.3	24.9	26.6	0.0	36.8	20.7	8.0	3.6	1.0
1994	86.3	28.5	45.8	0.0	2.6	4.7	3.0	0.2	0.8
1995	93.7	19.7	47.6	0.0	10.2	10.8	3.9	0.7	0.7
Ave.	100.9	22.1	41.9	0.0	16.0	11.6	7.0	1.6	0.9
Plot 14 (no-till)									
1990	118.8	20.5	51.4	0.0	23.1	4.2	11.6	8.0	3.5
1991	105.8	21.6	37.4	0.0	30.0	3.1	10.5	11.7	3.9
1992	84.4	15.1	47.7	0.0	10.9	3.7	4.9	1.9	1.7
1993	104.9	16.0	35.3	0.0	50.2	7.9	7.6	4.7	0.9
1994	76.9	26.8	35.3	0.0	10.5	5.5	4.4	0.8	0.8
1995	77.9	28.2	48.0	0.0	17.2	3.8	3.8	1.4	0.8
Ave.	100.9	21.4	42.5	0.0	23.7	4.7	7.1	4.8	1.9

P is precipitation; E is soil evaporation; T is crop transpiration; DS is deep seepage; TD is “tile” drain flow; LF is lateral flow; RO is runoff.

for the most part compared to observed data (Fig. 1c; Table 2). For example, 73% of the observed weekly differences and 100% of simulated differences were equal to or greater than zero (Fig. 1c). Ma et al. (2007c) deemed RZWQM adequate to simulate drain flow differences between tillage systems with 70% of annual simulated tillage differences in the same direction as observed (i.e., both observed and simulated treatment differences positive or negative). All (100%) of the annual simulated and observed drain flow were greater for the no-till plot (Table 2). The 7.7 cm/yr greater simulated tile drainage for the no-till plot was mostly due to 6.9 cm/yr less simulated subsurface lateral flow off the plot. The average annual simulated differences between plots for deep seepage, runoff, and ET were less than or equal to 0.3 cm/yr (Table 3). To investigate the RZWQM simulated water balance, we changed the lateral hydraulic conductivity (LKs) and lateral hydraulic gradient (LHG) of the tilled plot to that of no-till. This resulted in similar tile flow and lateral flow for the two tillage treatments (till average annual tile flow of 23.4 cm/yr and lateral flow of 4.1 cm/yr). Ma et al. (2007a) also showed that decreasing the LHG resulted in less lateral flow and more drain flow. Changing the macropore parameters of the tilled plot to that of no-till resulted in the drain flow to only decrease from 16.0 to 15.9 cm. In a single variable sensitivity analysis, Malone et al. (2004b) showed that individually increasing macropore radius and number of macropores (R_{mac} and N_{mac}) resulted in increased percolate and decreased runoff. For the current study, the macropore radius was greater for the no-till plot and the number of macropores was greater for the tilled plot (Table 1).

3.1.2. Atrazine in soil

The total soil profile atrazine for till and no-till plots were simulated with an EF of 0.79 and 0.64, respectively (Fig. 2). Among the greatest deviations between predicted and measured atrazine was for the no-till plot on June 23, 1992. Atrazine in soil was over predicted under no-till, partially because tillage was not simulated

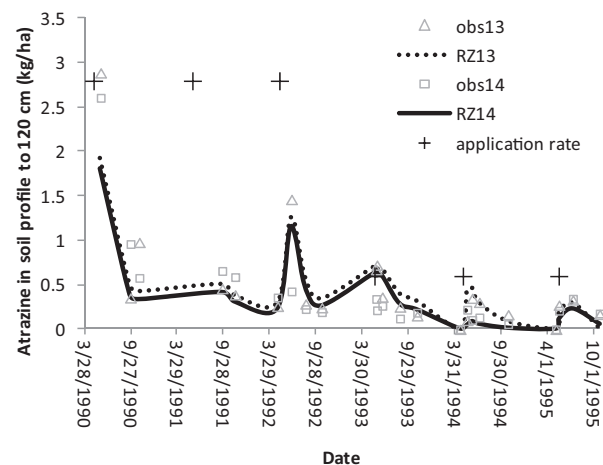


Fig. 2. Observed (obs) and RZWQM (RZ) atrazine in the soil profile. No atrazine was applied to plot 14 in 1994. Plot 13 is till and plot 14 is no-till.

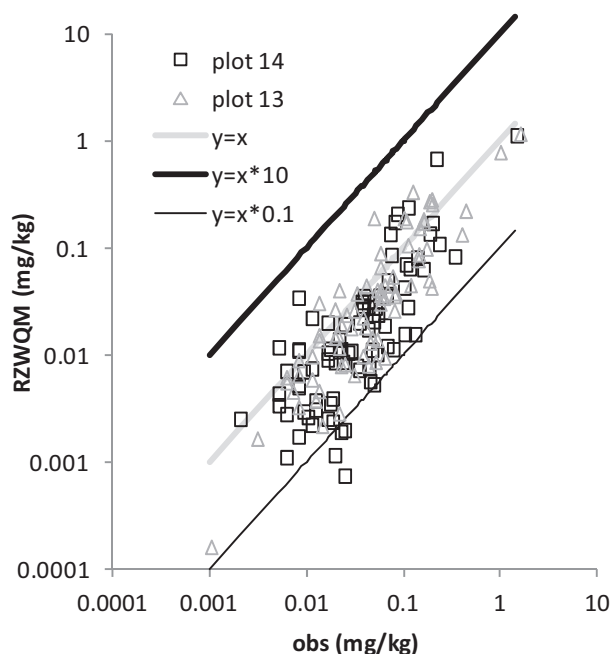


Fig. 3. Observed vs. RZWQM simulated atrazine concentration in the soil profile at different depth increments for plots 13 and 14 (1990–1995). Soil concentrations are not presented if observed values were less than 0.001 mg/kg. The two soil concentrations under predicted by more than a factor of 10 are for plot 14 (10–20 cm, May 1995; 0–10 cm, Oct. 1994). Plot 13 is tilled and plot 14 is no-till.

(as discussed in section 2.3.2). Without simulated tillage, simulated surface crop residue was nearly equal for the till and no-till plots. Atrazine is predicted to degrade considerably faster on crop residue with a default half life of 15 days compared to soil with a calibrated half life of 46 days (Table 1).

Soil concentrations at various depths through the profile on 21 specific dates from 1990 to 1995 were simulated within an order of magnitude of observed for the most part for both plots (Fig. 3). The lower concentrations are under predicted to a slightly greater degree than higher concentrations partly because pesticide degradation can slow down with time or be concentration dependant (e.g., Sarmah and Close, 2009). Sarmah and Close (2009) showed that atrazine dissipation in New Zealand soil slowed slightly during the first 120 d after application. Also, Weed et al. (1995) reported that a first order dissipation model underestimated the carryover of atrazine into the next growing season at this site near Nashua, Iowa. Atrazine was not applied to the no-till plot in 1994 resulting in soil atrazine concentrations to be under predicted by more than a factor of 15 on both October 28, 1994 for the 0–10 cm depth increment and May 17, 1995 for the 10–20 cm depth increment (Fig. 3). Atrazine was not applied to the no-till plot in 1995 until May 16.

3.1.3. Atrazine in drain flow

Fig. 1d and e shows the observed and simulated weekly flow weighted atrazine concentration in subsurface drain flow (FWAC) from 1990 to 1995 for the no-till and till treatments. For the no-till plot during the calibration years (1990–1992), 71% of simulated weekly FWAC were within a factor of 2 of observed and 84% within a factor of 5 when drainage was occurring and both observed and simulated concentrations were greater than zero. These simulation results are similar to Larsson and Jarvis (1999) where 66% of the simulated bentazone concentrations in tile drainage were within a factor of 2 of the measured values, and 89% within a factor of 5. Fig. 1d and e includes a performance index indicating when the ratio between observed and simulated atrazine concentration for a sampling event is less than two, between 2 and 5,

and greater than 5. For the no-till plot during the validation years (1993–1995), 94% of simulated weekly FWAC were within a factor of 2 of observed and 100% within a factor of 5 (Fig. 1d). The simulations were also very good for the tilled plot during 1993–1994 (84% within a factor 2 and 100% within a factor of 5; Fig. 1e), but less accurate for 1990–1992 (45% within a factor of 2 and 75% within a factor of 5). Most of the poor simulations for both plots were during 1990 (Figs. 1d and e), which could be partly due to variability in the atrazine application rate. In 1990 the reported application rate was 2.8 kg/ha on May 2 while the measured soil concentration on May 30 was nearly 2.8 kg/ha and the simulated soil concentrations were approximately 2 kg/ha (Fig. 2; an approximately 30% higher measured soil concentration than predicted). The annual average simulated tile drainage concentrations in 1990 were under predicted by approximately 20–40% (Table 2). Larsson and Jarvis (1999) comment that spatial variability of Bromide application may contribute to poor tile flow simulations. Despite several sampling events with inaccurate atrazine concentration simulations compared to observed data, the average annual FWAC was predicted within $\pm 0.3 \mu\text{g/L}$ of observed concentrations and the annual FWAC were simulated within a factor of two of observed concentrations every year (Table 2).

Although the model does not accurately reflect all the weekly concentration changes, the dynamics of cumulative atrazine flux in drainage for the calibration (1990–1992) and validation years (1993–1995) for the no-till plot are accurately simulated with an EF of 0.62 and 0.93, respectively (Fig. 1f). This is comparable to Branger et al. (2009), where an EF of 0.65 or less was reported for cumulative herbicide (isoproturon) flux in drainage and discussed as acceptable for pesticide simulations. The tilled plot cumulative atrazine fluxes were simulated accurately for 1990–1992 (EF = 0.90; Fig. 1f), but less accurately for 1993–1995 due to over predicted flux in 1993 that persisted through 1995 (EF = -2.76). The tilled plot over predicted cumulative atrazine flux in 1993 is because of an observed concentration recorded as 0.0 $\mu\text{g/L}$ for the 1993.7 sample, where the other five 1993.7 samples for the associated/replicated tilled and no-till plots (plots 22, 35, 31, 14, and 25) had concentration records ranging from 0.8 to 1.7 $\mu\text{g/L}$. The tilled plot simulated and observed cumulative atrazine fluxes for 1993.7 were 3.3 and 1.5 $\mu\text{g/L}$, respectively and for the previous sample period (1993.5) were 2.0 and 1.5 $\mu\text{g/L}$, respectively (Fig. 1f). Also, the average annual simulated atrazine flux was within $\pm 25\%$ of observed and within a factor of two of observed every year except for the tilled plot in 1995 when the concentrations were relatively low. This all suggests that the atrazine flux is simulated acceptably compared to observed data on an annual basis and cumulative weekly basis. Note that the annual atrazine flux reported in Table 2 cannot be calculated from the annual flow weighted atrazine concentrations and tile flow reported in Table 2 because the tile flow was computed using all data while the atrazine data was computed using only samples where the concentration was ≥ 0.5 ppb.

The model accurately responded to lower observed atrazine concentration in drain flow in 1993–1995 compared to 1990–1992 (Table 2), partly because atrazine application rates were lower from 1993 to 1995. Other reasons for the lower concentrations in the later years could be due to the rainfall patterns and the associated macropore flow characteristics, which are discussed below in Section 3.3. The no-till plot observed and simulated average annual FWAC for the model testing period (1993–1995) were 0.8 and 0.9 $\mu\text{g/L}$, respectively and for the calibration period (1990–1992) were 3.7 and 3.2 $\mu\text{g/L}$, respectively (Table 2). Therefore, the no-till plot observed and simulated FWAC ratios between 1990–1992 and 1993–1995 were both approximately 4 (Table 2; $3.7/0.8 = 4.6$; $3.2/0.9 = 3.6$).

The model accurately responded to lower observed atrazine concentration in the tilled plot compared to the no-till plot

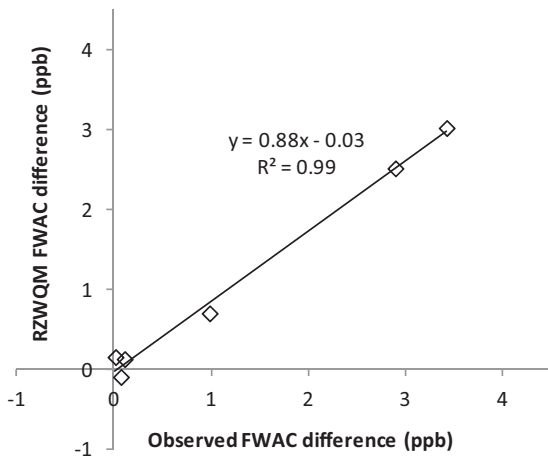


Fig. 4. Annual flow weighted atrazine concentration (FWAC) difference (ppb) in subsurface drain flow between plots 14 (no-till) and 13 (till).

(Table 2). The average annual observed and simulated FWAC differences between the no-till and tilled plots were 1.3 and 1.1 $\mu\text{g/L}$, respectively (Table 2; e.g., $2.3 - 1.0 = 1.3 \mu\text{g/L}$). The simulated and observed annual FWAC differences between the no-till and tilled plots were less during the low atrazine application years compared to the high application years. For 1993–1995 the average observed and simulated differences were 0.1 and 0.1 $\mu\text{g/L}$, respectively and for 1990–1992 the observed and simulated differences were 2.4 and 2.1 $\mu\text{g/L}$, respectively. Furthermore, the model accurately simulated the annual FWAC difference each year between the no-till and tilled plots compared to the observed data (Fig. 4; $R^2 = 0.99$; slope = 0.88; $n = 6$; Table 2).

3.2. Model parameter discussion

The calibrated surface crust and surface soil hydraulic conductivities (K_s) were nearly equal for the till and no-till plots while the macropore radius (R_{mac}) was slightly greater for no-till (Table 1). The calibrated number of “active” macropores (i.e., half of percolate producing) was less for no-till ($0.5 \cdot N_{\text{mac}}$; Table 1; 0.01 and 0.017 cm^{-2}). Kumar et al. (1998) also report greater N_{mac} under moldboard tillage than no-till. The calibrated values of these parameters between the two plots also correspond to previous RZWQM assessments under different tillage systems (Malone et al., 2003, 2004b). The greater N_{mac} for till resulted in more of the soil matrix contributing to pesticide sorption (WVOL) resulting in lower pesticide transport through macropores (Eq. (2); Fig. 5;

Malone et al., 2004a). Malone et al. (2004a) discussed that less herbicide can leach with greater N_{mac} because water and chemicals transported into macropores are distributed between more macropores than with smaller N_{mac} . Therefore, more soil was available for chemical partitioning per mass of chemical for the tilled plot. The greater R_{mac} for the no-till plot compared to the tilled plot only slightly increased the soil matrix contributing to pesticide sorption (WVOL), and the effect of R_{mac} on WVOL was dwarfed by N_{mac} (Fig. 5). It should be noted that under some conditions R_{mac} can have a very large effect on pesticide transport through macropores because greater R_{mac} can result in a much larger volume of macropore flow (Malone et al., 2004b). Expounding on the contributions of R_{mac} and N_{mac} to WVOL, the WVOL of the till and no-till plots were 0.026 and $0.016 \text{ cm}^2/\text{cm}^2$, respectively (Eq. (2); Fig. 5). Under the conditions of this study, the relative composite sensitivity values (RCS) also suggest that FWAC is more sensitive to N_{mac} than to R_{mac} and the RCS value of N_{mac} is greater than atrazine half life ($t_{0.5}$) (Table 1).

The lateral hydraulic conductivity and lateral hydraulic gradient (LKs and LHG) were less sensitive than the macropore parameters for affecting FWAC. Changing the LKs and LHG of the tilled plot to that of no-till resulted in the average annual mass transport of atrazine in tile drainage to increase from 1.6 to 2.1 g/ha but the average annual FWAC remained constant at $0.9 \mu\text{g/L}$ (Table 3). Note that the simulated average annual atrazine loss and FWAC of Tables 2 and 3 were different for the same plot because the values reported in Table 2 were computed using simulated concentrations $\geq 0.5 \mu\text{g/L}$ and only included data when observed samples were collected while Table 3 uses all RZWQM simulated data. Decreasing the LKs of the tilled plot by a factor of 2 without changing other parameters resulted in the average annual FWAC to only increase slightly (to $1.0 \mu\text{g/L}$). Changing the tilled plot N_{mac} and R_{mac} to that of no-till while keeping the other parameters constant resulted in the average annual mass transport of atrazine in tile drainage to increase from 1.6 to 5.1 g/ha and the average annual FWAC to increase from 0.9 to $3.0 \mu\text{g/L}$. Therefore, the LKs and LHG have little effect on the FWAC under the simulated conditions but the macropore parameters greatly affect FWAC. Also, the RCS values suggest that FWAC was less sensitive to LKs and LHG than to N_{mac} with the sensitivity order of selected RZWQM input parameters: $K_{\text{oc}} > N_{\text{mac}} > t_{0.5} > R_{\text{mac}} > \text{LHG} > \text{LKs}$ (Table 1).

In 1990 atrazine was applied on May 2. After atrazine application, the first storm with substantial simulated atrazine transport into macropores occurred on May 19, 1990 when 6.0 cm of rainfall was recorded and 3.3 and 3.5 cm of overland flow were simulated to enter macropores for the till and no-till plots, respectively (Fig. 6a). Macropore flow detailed output for this storm with 3 kg/ha of atrazine applied each year to both plots revealed that 246 and 175 g/ha atrazine was simulated to enter macropores for the till and no-till plots, respectively (Fig. 6b). Although till had 71 g/ha more atrazine enter macropores partly because of lower surface soil pore size distribution index (PSD; Malone et al., 2003), it had 124 g/ha more sorption to macropore walls on surface 40 cm of soil mostly because of higher N_{mac} (Figs. 5 and 7; Table 1). The water table was rarely shallower than 40 cm below the soil surface in 1990 (Fig. 6d), reducing movement of atrazine into drain water. This is in contrast to Malone et al. (2003) where the no-till treatment had more atrazine enter macropores and leach to 30 cm due to lower infiltration capacity in the 8–30 cm soil depth causing faster initiation of macropore flow. The atrazine entering macropores that did not leach to the tile drain depth and was not sorbed to walls entered matrix soil through lateral capillary flow. The RCS values suggest that FWAC was more sensitive to N_{mac} and R_{mac} than to the saturated hydraulic conductivity (K_s) of the surface soil layer and surface crust hydraulic conductivity (Table 1).

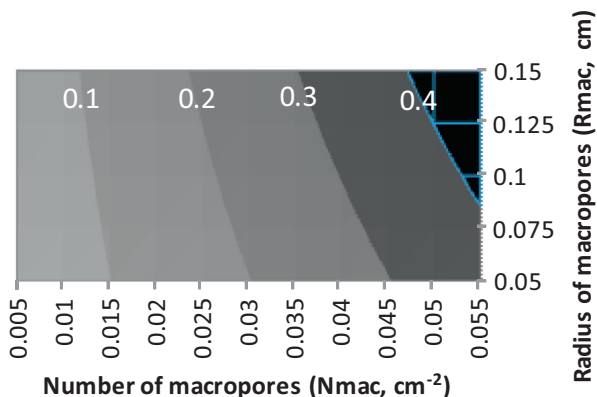


Fig. 5. Soil volume surrounding macropores available for sorption of atrazine per total soil volume at each depth increment as described by Eq. (2) (WVOL; cm^2/cm^2).

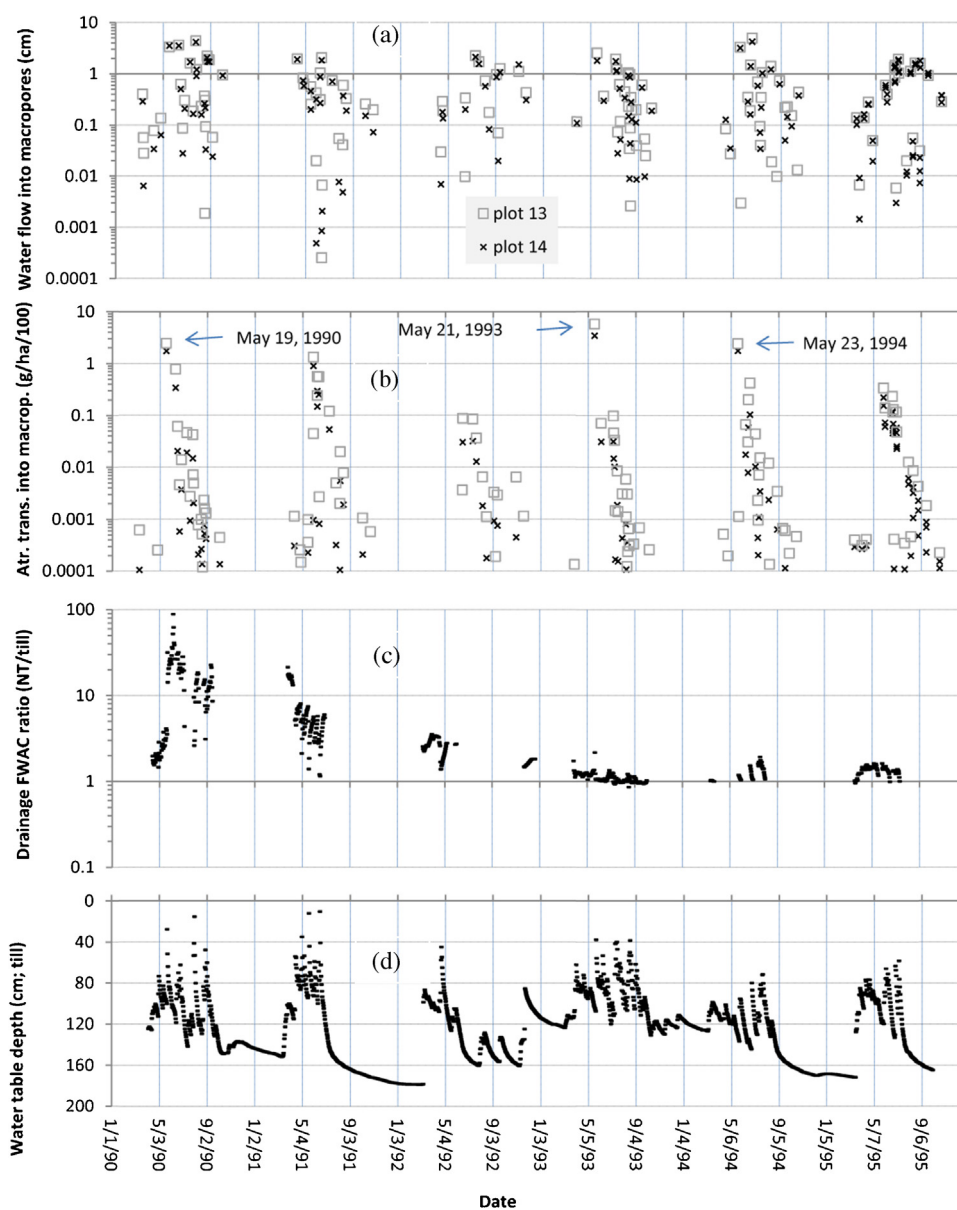


Fig. 6. RZWQM daily water table depth, atrazine concentration ratio in drain flow, and macropore flow characteristics. Atrazine was spring applied each year at a rate of 3 kg/ha for both plots 13 and 14. (a) is daily water flow into macropores. (b) is daily atrazine transport into macropores. (c) is daily flow weighted atrazine concentration (FWAC) ratio in drain flow (NT/till). (d) is daily water table depth for plot 13. Plot 13 is till and plot 14 is no-till (NT).

Kumar et al. (1998) attributed the greater atrazine transport under no-till compared to tilled systems to greater LKs; however, atrazine concentrations and LKs were not included in the sensitivity analysis and the reasons for greater atrazine concentrations in the no-till plot were not clear. In the current study, the sensitivity analysis was based on atrazine concentrations in drain flow and all PEST optimized parameters were included. In contrast to greater RZWQM simulated pesticide transport to subsurface soil with fewer “active” macropores (e.g., Malone et al., 2001, 2004b), the RZWQM sensitivity analysis of Kumar et al. (1998) found greater simulated atrazine transport to subsurface drains/soil with greater macroporosity, perhaps because of greater overland flow simulated to enter macropores. However, the no-till plots were parameterized with a smaller macroporosity than the tilled plots by Kumar et al. (1998). Similar to Malone et al. (2001, 2004b), the sensitivity analysis of Kumar et al. (1998) found that a smaller K_s of the surface soil resulted in greater pesticide transport to subsurface drains/soil but

the no-till plots were parameterized with a greater surface layer K_s than the tilled plots.

3.3. RZWQM simulated atrazine concentrations in drainage under different application rates and tillage

As shown above in Section 3.1.3, both the observed and simulated results suggest that the FWAC difference between plots was less for the later period (1993–1995) compared to the earlier period (1990–1992). The reason for this difference between periods, however, still needs to be addressed. For example, was it due to different atrazine application rates, different weather conditions, or the absence of atrazine application to the no-till plot in 1994? Therefore, we simulated atrazine transport in drain flow with atrazine applied at constant rates every year to both tillage treatments using the optimized RZWQM (Table 1). To investigate the effect of application rates on atrazine concentration in drain

Table 4
RZWQM simulated annual flow weighted atrazine concentrations (FWAC, $\mu\text{g/L}$) at four different application rates (0.5, 1.0, 2.0, and 3.0 kg/ha) for the two tillage systems.^a

Year	Till				No-till			
	Annual atrazine application rate (kg/ha)							
	0.5	1	2	3	0.5	1	2	3
FWAC ($\mu\text{g/L}$)								
1990	0.1	0.2	0.5	0.7	0.6	1.2	2.5	3.7
1991	0.3	0.5	1.1	1.6	0.7	1.4	2.8	4.2
1992	0.2	0.3	0.7	1.0	0.3	0.6	1.2	1.8
1993	0.2	0.5	1.0	1.4	0.2	0.5	0.9	1.4
1994	0.2	0.4	0.7	1.1	0.2	0.5	0.9	1.4
1995	0.2	0.5	0.9	1.4	0.3	0.6	1.3	1.9
Average FWAC over several years ($\mu\text{g/L}$)								
1990–1992	0.2	0.4	0.7	1.1	0.5	1.1	2.2	3.3
1993–1995	0.2	0.4	0.9	1.3	0.3	0.5	1.0	1.6
1990–1995	0.2	0.4	0.8	1.2	0.4	0.8	1.6	2.4
Average FWAC/atrazine application rate (e.g., $2.41/3 = 0.80$; $1.61/2 = 0.80$)								
1990–1992	0.37	0.37	0.37	0.37	1.08	1.08	1.08	1.08
1993–1995	0.44	0.44	0.44	0.44	0.53	0.52	0.52	0.52
1990–1995	0.40	0.40	0.40	0.40	0.80	0.80	0.80	0.80

^a Annual drain flow for each plot was the same as Table 3 except plot 14 (no-till) had 5.7 and 14.7 cm of drainage for 1994 and 1995, respectively due to corn planting in 1994. Drain flow was not affected by atrazine application rate.

flow, we ran the model under four different application rates with constant rates applied every year.

Applying constant atrazine application rates each year to each plot resulted in a proportional increase in overall FWAC ($\mu\text{g/L}$) with increasing atrazine application rates. The FWAC is equal to $0.40 \times \text{rate}$ for the tilled plot and $0.80 \times \text{rate}$ for the no-till plot ($R^2 = 1.00$; Table 4, bottom row). Therefore, the FWAC for the no-till plot was twice that of the tilled plot for each atrazine application rate over the time period (1990–1995). However the difference between tillage systems was more pronounced in the early period, with no-till/till FWAC ratios of 3.0 and 1.2 for 1990–1992 and 1993–1995, respectively (e.g., $3.3/1.1 = 3.0$, for the high application rate; Table 4). These ratios were constant among each of the four application rates. This suggests that the weather contributed to the early (1990–1992) and late period (1993–1995) tillage system effects on FWAC.

The characteristics of storms that drive relatively large quantities of atrazine to macropores may affect FWAC differences between tillage systems and time periods (1990–1992 and 1993–1995). Large storms shortly after pesticide application drive pesticide transport to macropores because smaller storms wash

pesticide into the soil matrix where it is less available for transport to macropores (Shipitalo et al., 1990). The rapid and direct transport of pesticides in macropores to drainage systems may occur infrequently (only every few years) under spring application (Lewan et al., 2009). Therefore, we investigated the macropore flow details of a few large storms with annual atrazine application rates of 3 kg/ha for each plot.

The first instance of the daily FWAC ratio between the no-till and till plots exceeding 10 was on May 20, 1990 (no-till/till), which was the first large movement of atrazine into macropores (Fig. 6b and c). The relatively large FWAC ratio persisted into 1991 where the ratio remained above 10 through April 6 then dropped to 4.8 when tiles began flowing again for both plots on April 12. Some details of the RZWQM simulated macropore flow associated with this storm were described in Section 3.2.

The largest storm over all six years transporting atrazine into macropores occurred on May 21, 1993 (Fig. 6b). However, this storm did not result in as large a FWAC ratio as 1990. Part of the reason for this is the timing and characteristics of macropore flow resulted in little atrazine transport in macropores below 40 cm (Fig. 7). One of these characteristics includes the average atrazine concentrations entering macropores, which were 2256 and 1916 $\mu\text{g/L}$ for the till and no-till treatments, respectively. These concentrations were more than three times greater than the May 19, 1990 storm resulting in more than twice the atrazine sorption to macropore walls in the surface 40 cm of soil (Fig. 7). Atrazine sorption to the surface 40 cm of soil for the till and no-till plots were 568 and 334 g/ha, respectively. Total atrazine movement into macropores was 573 g/ha and 343 g/ha, respectively for the till and no-till plots, with 2.54 and 1.79 cm of overland flow. Therefore, little atrazine moved below 40 cm and the water table never rose above 38 cm from the soil surface in 1993 (Fig. 6d), which contributed to a small FWAC ratio in 1993 compared to 1990.

The tiles were not draining for the intense storm driving over 200 g/ha atrazine into macropores on May 23, 1994 (Fig. 7b). The relatively large storm on June 23, 1994, however, resulted in 42 g of simulated atrazine to enter macropores for the tilled plot which contributed to the increased FWAC ratio (from approximately 1.1 in May to 1.5 on June 23).

These results illustrate the complex interactions between rainfall patterns, macropore flow, tillage, and pesticide losses in subsurface drainage. The review article by Reichenberger et al. (2007) stated that “the limited amount of available literature

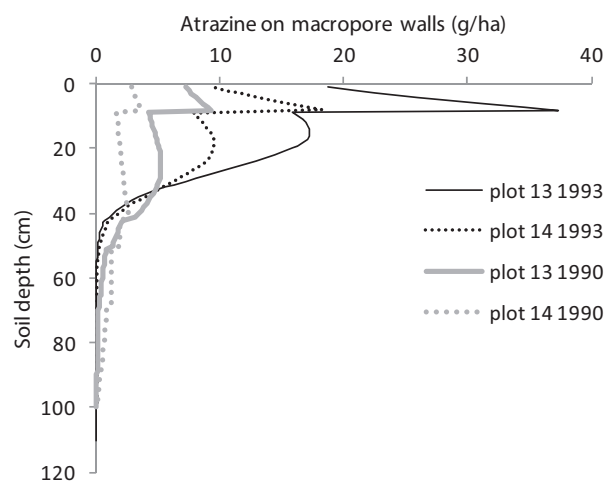


Fig. 7. RZWQM simulated atrazine sorbed to macropore walls at the end of rainfall on May 19, 1990 and May 21, 1993 for plots 13 (till) and 14 (no-till). Atrazine application rate was 3 kg/ha on May 2, 1990 and May 17, 1993.

suggests that the effects of . . . tillage operations . . . on pesticide losses via drainage and leaching are insufficiently known and at best unpredictable". The complexity of this subject requires more research; however, our results suggest that RZWQM can accurately predict the effects of tillage systems on pesticide losses via drainage under a range of rainfall conditions and high and low atrazine application rates.

4. Summary and conclusions

The results of this study along with the earlier study by Kumar et al. (1998) suggest that RZWQM can generate realistic simulations of pesticide transport to subsurface drains under different tillage systems. The current study also suggests that the model can accurately simulate atrazine transport to subsurface drains under different application rates for six years of weather conditions (1990–1995). Part of the observed atrazine concentrations in subsurface drain flow were used for model calibration and the last three years of data from the no-till plot were reserved for model testing.

The calibrated model parameters were reasonable compared to measurements at the site and literature sources. The number of "active" macropores was a sensitive input parameter that was calibrated to be greater for the tilled plot compared to the no-till plot, which confirms that a greater number of "active" macropores per unit area results in more soil available for pesticide sorption (Malone et al., 2004a). The number of macropores was the second most sensitive parameter affecting pesticide concentration in subsurface drain flow while the atrazine partition coefficient was the most sensitive parameter.

Both the observed and simulated results suggest that the atrazine concentrations in subsurface drain flow were greater for the no-till plot compared to the tilled plot. Our simulation results suggest this difference was mostly because of the number of macropores per unit area. Both the observed and simulated drain flow atrazine concentration differences between tillage systems were greater during the first three years of the experiment (1990–1992) when atrazine application rates were greater compared to the last three years (1993–1995). Our modeling results suggest this difference between periods is partly due to macropore flow characteristics. The last three years of observed data were obtained under lower atrazine application rates, lack of atrazine application to the no-till plot in 1994, along with different rainfall characteristics. These factors complicated interpretation of the year-to-year observed differences. Our simulations with four different atrazine application rates (0.5, 1.0, 2.0, and 3.0 kg/ha) suggest that applying a constant atrazine rate each year to each plot resulted in (1) a linear increase of flow weighted atrazine concentration (FWAC) with increasing application rates, (2) FWAC for the no-till plot was twice that of the tilled plot over the six year simulation period, and (3) the difference between tillage systems was greater during the first three years of the experiment than the last three years partly due to the characteristics of macropore flow during large storms.

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